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Short communication

Facile synthesis of 3D silicon/carbon nanotube capsule composites as anodes for high-performance lithium-ion batteries

Xinyang Yue [a], Wang Sun [a, **], Jing Zhang [a], Fang Wang [a], Kening Sun [a, b, *]

[a] Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemical Engineering and Environmental, BIT-QUB Joint Center on Novel Energy and Materials Research, Beijing Institute of Technology, Beijing, 100081, People's Republic of China
[b] Collaborative Innovation Center of Electric Vehicles in Beijing, No. 5 Zhongguancun South Avenue, Haidian District, Beijing, 100081, People's Republic of China

HIGHLIGHTS

- 3D Si/CNCs with a hollow nanostructure was synthesized by W/O emulsion technique.
- The 3D Si/CNCs can effectively solve the volume expansion problem.
- Si/CNCs exhibit a high capacity of 1226 mAh g^{-1} at 0.5 A g^{-1} over 100 cycles.
- An excellent rate capability of 547 mAh g^{-1} can be attained at 10 A g^{-1}.

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ABSTRACT

Carbon nanotubes have attracted widespread attention as ideal materials for Lithium-ion batteries (LIBs) due to their excellent conductivity, mechanical flexibility, chemical stability and extremely large surface area. Here, three-dimensional (3D) silicon/carbon nanotube capsule composites (Si/CNCs) are firstly prepared via water-in-oil (W/O) emulsion technique with more than 75 wt% loading amount of silicon. CNCs with unique hollow sphere structure act as a 3D interconnected conductive network skeleton, and the cross-linked carbon nanotubes (CNTs) of CNCs can effectively enhance the strength, flexibility and conductivity of the electrode. This Si/CNCs can not only alleviate the volume expansion, but also effectively improve the electrochemical performance of the LIBs. Such Si/CNCs electrode with the unique structure achieves a high initial discharge specific capacity of 2950 mAh g^{-1} and retains 1226 mAh g^{-1} after 100 cycles at 0.5 A g^{-1}, as well as outstanding rate performance of 547 mAh g^{-1} at 10 A g^{-1}.

1. Introduction

Recent developments of intelligent electronic devices and electric vehicles have increased the demands for lithium-ion batteries (LIBs) with longer service lives and higher power capacities [1–3]. Silicon is one of the most promising potential candidates as a substitute for graphite due to its high theoretical specific charge capacity of 4200 mAh g^{-1} (as $Li_{22}Si_5$ or $Li_{15}Si_4$), which is ten-times higher than that of graphite. The low work potential and natural abundance make silicon a safer and more commercially viable electrode material for LIBs [5,6]. Unfortunately, the large volume changes (~400%) during lithium insertion and extraction result in the collapse of electrode networks and the exfoliation of active materials from the current collector, which cause poor electrochemical performance that fall short of consumer demands [7–9].

In order to overcome these challenges, many efforts and improvements have been made in the past decades, including micro/nanostructured silicon materials [10–14] and silicon-carbon nanocomposites, such as silicon-graphene [15], silicon-hollow carbon spheres [16], silicon-carbon nanofibers [17], silicon-carbon nanotubes [18–23]. These carbon materials all can improve the electronic conductivity of the Si electrode, and can be used as a soft

* Corresponding author. Beijing Key Laboratory for Chemical Power Source and Green Catalysis, School of Chemical Engineering and Environmental, BIT-QUB Joint Center on Novel Energy and Materials Research, Beijing Institute of Technology, Beijing, 100081, People's Republic of China.
** Corresponding author.
E-mail addresses: sunwang@bit.edu.cn (W. Sun), bitkeningsun@163.com (K. Sun).

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medium to buffer the stress of volume expansion during charge/discharge processes.

Carbon nanotubes (CNTs) are promising electrode materials for LIBs because of their excellent conductivity, mechanical flexibility, chemical stability and extremely large surface area [24]. Therefore, the combination of the high capacity of Si with these unique properties of CNTs will lead to the formation of better electrodes for LIBs. For example, a uniform MWCNT@Si nanocomposite had been prepared via the magnesiothermic reduction of pre-synthesized MWCNT@SiO2 nanocables, and showed high reversible capacity and good cycling performance [23]. A core/shell type Si/CNTs composite had been prepared by electroless deposition, which can allow volume expansion of Si core without severe electrode swelling [19]. Inspired by these works, we proposed 3D Si/CNCs with unique hollow structure, and the Si/CNCs were successfully prepared by water-in-oil (W/O) emulsion technique. A castor oil-based emulsion was used with ammonia water as the dispersion phase and Tetraethyl orthosilicate (TEOs) as silicon sources for the production of Si/CNCs. Fig. 1 gives an overview of the synthesis procedure of the 3D Si/CNCs. CNCs were formed by the self-assembly technique of coating W/O droplets with MWCNTs [25,26]. And we herein try to synthesize Si nanoparticle dispersed uniformly in the 3D interconnected conductive network of CNCs and keep the unique hollow sphere structure of Si/CNCs by controlling the amount of TEOs. The water in the shell was removed to create hollow structure, and the Si/CNCs were synthesized via a typical magnesiothermic reaction.

Within this work, the electrochemical performance of LIBs with different anodes has been studied. From this it was observed that the 3D Si/CNCs can significantly improve the reversible capacity and the cycling stability of LIBs, mainly because of the significant enhanced conductivity and structural durability. Particularly, the 3D interconnected conductive network of CNCs and the unique hollow sphere structure of Si/CNCs can effectively alleviate the volume expansion and improve the electrochemical performance of the LIBs. Furthermore, TEOs is a lower cost silicon resource than Si nanoparticles, and Si/CNCs prepared with these affordable, environmentally friendly raw materials and methods are good candidates for anodes in LIBs.

2. Materials and methods

2.1. Preparation of CNCs

The MWCNTs (Shenzhen Nanoport Co. China) with diameter of 40–60 nm and length of 0.5–500 μm were pretreated with a mixture of concentrated nitric acid (67%) and sulfuric acid (98%) (H_2SO_4/HNO_3 = 3/1 (v/v)) at 60 °C bath for 12 h under the reflux condensation, then collected by vacuum filter and washed with deionized water until the filtrate is neutral. The oxidation products were dried at 80 °C for 12 h. 100 mg modified MWCNTs were dispersed in the mixture solution of 15 ml ammonia water and 5 ml deionized water under the ultrasonic for 3 h at 25 °C. After dispersion, the suspension was poured into a glass flask containing 80 ml castor oil preheated to 40 °C and intensely stirred for 1 h at 40 °C.

2.2. Preparation of SiO_2/CNCs

TEOs was slowly added into this emulsion and still stirred for 1.5 h at 40 °C. After the formation of silica, the bath temperature was adjusted to 90 °C under the vigorous stirring for 1 h to remove the water. After the emulsion was cooled to room temperature, the resulting of SiO_2/CNCs were collected by centrifugation and washed 5 times using petroleum ether to remove the castor oil, followed by air drying at 80 °C for 24 h. Different amount of TEOs (0.5 mL, 3 mL, and 6 mL) was used, these samples were denoted as Si/CNCs-0.5, Si/CNCs-3, and Si/CNCs-6.

2.3. Preparation of Si/CNCs

100 mg SiO_2/CNCs and 150 mg magnesium powder (Aladdin AR 99.5%) were put in a corundum boat and heated in a tube furnace at 700 °C for 6 h under an Ar atmosphere. The as obtained particles were firstly immersed in 1 M HCl for 6 h to remove the side products then immersed in 5 wt% HF solution for 1 h to get rid of silica. The final products (Si/CNCs) were collected by centrifugation and washed 3 times using deionized water followed by vacuum drying at 80 °C for 12 h.

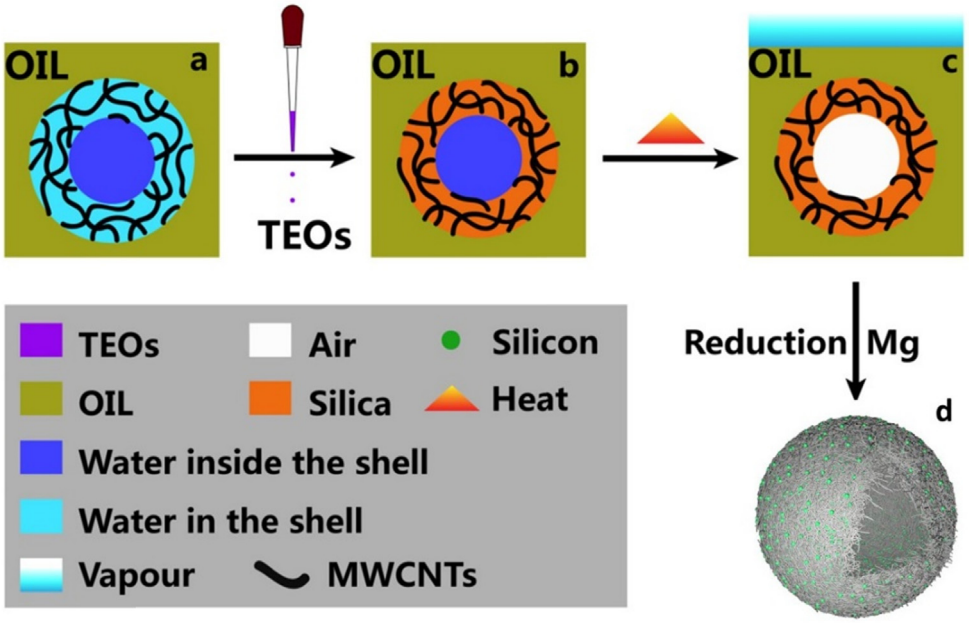

Fig. 1. Schematic illustration of the 3D Si/CNCs.